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(34) NON-AQUEOUS SECONDARY BATTERY

(51)Abstract:

PROBLEM TO BE SOLVED: To improve energy quantity of a lithium secondary battery, and improve the cycle lifetime thereof by forming the battery out of a positive electrode having positive electrode active material as a transition metal oxide capable of absorbing and releasing lithium; a negative electrode having negative electrode material using the compound including a silicon atom; and the non-aqueous electrolyte.

SOLUTION: A positive electrode having positive electrode active material LiCoO₂ as a transition metal oxide capable of absorbing and releasing lithium and a mixture material of acetylene black and polyvinylidene fluoride is manufactured. A negative electrode having negative electrode material of the alloy including a silicon atom and having 0.01-50 µm of mean grain size and including at least one kind or more of alkali earth group metal, transition metal and semimetal is manufactured.

Furthermore, the colorless electrolyte having a specific gravity of 1.135 and formed by dissolving ethylene carbonate in the diethyl carbonate little by little and dissolving LiBF₄ and LiPPb in order is filled between the positive electrode and the negative electrode. With this structure, the discharging capacity, energy quantity and cycle lifetime are improved.

EXTRACT S

PO and DMU1 are the abbreviations for say
changes caused by the use of these translations.

1 This document has been translated by computer. So the translation may not reflect the original precisely.

2 *** shows the word which can not be translated.

3 In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]In a nonaqueous secondary battery which makes a component an anode which has positive active material, a negative electrode which has a negative pole material, and nonaqueous electrolyte, A nonaqueous secondary battery, wherein the positive active material is a transition metal oxide in which insertion discharge of lithium is possible and this negative pole material is a compound containing a silicon-alum in which insertion discharge of lithium is possible.

[Claim 2]The nonaqueous secondary battery according to claim 1, wherein a mean grain size of this silicon compound is 0.01-50 micrometers.

[Claim 3]The nonaqueous secondary battery according to claim 1 or 2, wherein this silicon compound is an alloy.

[Claim 4]The nonaqueous secondary battery according to any one of claims 1 to 3, wherein this silicon compound is the silicon which removed metal from a metal-silicide

[Claim 5]The nonaqueous secondary battery according to any one of claims 1 to 4, wherein this silicon compound has adhered with ceramics which do not react to lithium.

[Claim 6]The nonaqueous secondary battery according to any one of claims 1 to 5, wherein this silicon compound is covered with metal at least,

[Claim 7]The nonaqueous secondary battery according to any one of claims 1 to 6, wherein this silicon compound is beforehand covered with thermoplastics,

[Claim 8]The nonaqueous secondary battery according to any one of claims 1 to 7 being carbon together 5 to 1900% by a weight ratio to this silicon compound.

[Claim 9]The nonaqueous secondary battery according to any one of claims 1 to 8 if the charge-and-discharge range of this silicon compound is expressed with Li_xSi to silicon as equivalent ratio of lithium which carries out insertion discharge, wherein x is within the limits of 4.2 or less [17 or more];

[Claim 10]This positive active material = Li_xMnO₂ (M=Cu and nickel → 1 Fe and 1 Al least one part of Mn, a compound expressed with y=0.1-2, or a compound which has the layered structure expressed with Li_yNi₂O₂ (y=Mn 2 or 2); ** = the nonaqueous secondary battery according to any one of claims 1

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No 9 using one-set even if small.

{Translation done}

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the invention]

[0001]

[Field of the invention] This invention relates to the long-life lithium secondary battery of a cycle life with a non-aqueous secondary battery, especially high capacity.

[0002]

[Description of the Prior Art] The lithium contained in positive active material is first inserted in a negative pole material, and the activity of a negative pole material is raised in the lithium secondary battery using the negative pole material which does not contain a lithium metal, and the positive active material containing lithium. This is a charge reaction and the reaction which makes a lithium ion insert in negative active material from the reverse negative pole material is a discharge reaction. Carbon is used as this type of a lithium cell negative pole material. The theoretical capacity of carbon (C_6) is 372 mAh/g, and further high capacity negative pole material is desired. On the other hand, the theoretical capacity of the silicon which forms lithium and an intermetallic compound surpasses 4000 mAh/g, and it is known well that it is larger than that of carbon. For example, silicon of a single crystal is indicated in JP,5-74463,A, and amorphous silicon is indicated in JP,7-29812,A. In the alloy having contained silicon, the example which contains silicon in Li-aluminum alloy is indicated by JP,63-08369,A (silicon is 19 % of the weight), and 63-174275 (silicon is 0.08 to 1.0 % of the weight), and the 63-098665 (silicon is 1 to 5 % of the weight). However, since each of such alloy patent application made lithium the subject, the compound which does not contain lithium was used for positive active material. In JP,4-108662,A, 0.05 to 1.0% of the weight of the alloy is indicated for silicon. In JP,62-226663,A, the method of mixing graphite powder with lithium and the metal in which an alloy is possible is indicated. However, it has not come to us by all being inferior in a cycle life. As a reason which is inferior in the cycle life of silicon, volume expands by that the electron conductivity is low and lithium insertion, and it is guessed that pulverization of the particles is derived out.

[Problem] to be Solved by the invention] The purpose of this invention is to raise the amount of

energy of a Minimum Secondary Battery, and to raise a cycle life from:

[Means for Solving the Problem] In a nonaqueous secondary battery made into a component, a terminal portion of this invention an anode which has positive active material; a negative electrode which has a negative pole material; and nonaqueous electrolyte this positive active material, it is a transition metal oxide containing lithium, and has solved with a nonaqueous secondary battery using a compound containing a silicon atom as this negative pole material.

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[Embodiment of the Invention] Although the mode of this invention is explained below, the invention is not limited to these.

- (1) The nonaqueous secondary battery which the positive active material is a transition metal oxide which can carry out insertion discharge of the lithium, and is characterized by using the compound containing a silicon atom as the negative pole material in the nonaqueous secondary battery which makes a nonporous the anode which has positive active material, the negative electrode which has negative pole material, and nonaqueous electrolyte.

(2) The nonaqueous secondary battery whose mean grain size of the silicon compound of a paragraph (1) is 0.01-50 micrometers.

(3) The nonaqueous secondary battery whose silicon compound of a paragraph (1) is an alloy.

(4) The nonaqueous secondary battery whose at least one sort of metal other than silicon is all-stone-earth metals, a transition metal, and scandium in the alloy of a paragraph (3).

(5) The nonaqueous secondary battery whose at least one sort of a paragraph (3) or the metal of (4) is germanium, Si, Ag, aluminum, Au, Cd, Ga, In, Sb, Sn, and Zn.

(6) The nonaqueous secondary battery which contains at least one sort chosen from Mg, Fe, nickel, Cr, Ti, Mo, and W in a paragraph (5).

(7) The nonaqueous secondary battery whose atomic ratio to silicon of the metal indicated in a paragraph (6) is 20% or less exceeding it.

(8) Paragraph (2) Nonaqueous secondary battery whose atomic ratio of this metal to silicon given in (7) is 5 to 80%.

(9) Paragraph (3) Nonaqueous secondary battery produces by (8) by the alloy of a statement calculating.

(10) The nonaqueous secondary battery whose calcination temperature is not less than 1600 °C and 1803 °C series in a paragraph (9).

(11) The nonaqueous secondary battery whose cooling temperature after calcination of an alloy is about by 10 °C in a paragraph (9) or (10).

(12) The nonaqueous secondary battery which is the silicon in which the silicon compound of the statement removed metal from the metal chloride in the paragraph (1).

(13) The nonaqueous secondary battery whose metal nitride given in a paragraph (12) is a lithium nitride.

- (14) The nonaqueous secondary battery whose lithium content of a lithium-nitride given in a paragraph (13) is 100-62.6atom% to silicon.

(15) The nonaqueous secondary battery which is the edition from which lithium was removed by processing a lithium-aluminum alloy in the alcohol which the silicon compound of the statement dried in the paragraph (1);

(16) The ceramics to which a silicon compound given in a paragraph (9) does not react to leave, and so adhering nonaqueous secondary battery.

(17) The nonaqueous secondary battery which is at least one sort as which ceramics given in a paragraph (16) are chosen from aluminum₂O₃, SiO₂, TiO₂, SC, and Si₃N₄.

(18) The nonaqueous secondary battery whose ceramics given in a paragraph (17) are SiO₂.

(19) The nonaqueous secondary battery whose SiO₂ given in a paragraph (18) is SiO₂ or colloid.

(20) Paragraph (16) Nonaqueous secondary battery whose weight ratio of these ceramics to a silicon compound given in - (19) is 2 to 90%.

(21) Paragraph (16) Manufacturing method of the nonaqueous secondary battery with which the method of making these ceramics adhere to the silicon compound of a statement includes the process heated below not less than 300 °C to 1600 °C in - (20).

(22) The nonaqueous secondary battery with which the silicon compound given in a paragraph (1) is covered by at least one sort of metal.

(23) A manufacturing method of the nonaqueous secondary battery which is at least one sort as which the method of making it cover with the metal of a paragraph (22) is chosen from a nonelectrolytic melting method, vacuum deposition, sputtering process, a chemical-vapor-deposition method, and the metal-pushing method.

(24) The nonaqueous secondary battery whose metal with which the paragraph (22) and (23) is covered is at least one sort of nickel, Cu, Ag, Co, Fe, Cr, W, Ti, Au, Pt, Pd, Sn, and Zn.

(25) The nonaqueous secondary battery whose metal with which the paragraph (22) and (23) is covered is at least one sort of Nickel, Cu, and Ag.

(26) Paragraph (22) Ten or more times [\times] of the specific conductance of the silicon compound with which the specific conductance of the silicon compound covered with the metal of - (25) is not covered] the nonaqueous secondary battery.

(27) Paragraph (22) Nonaqueous secondary battery whose coating volume of the metal of - (26), is 1-100atom% to silicon.

(28) The nonaqueous secondary battery with which the silicon compound of the paragraph (1) is beforehand covered selectively by thermoplastics.

(29) A manufacturing method of the nonaqueous secondary battery whose how to cover a paragraph (28) with thermoplastics selectively beforehand is a method including the process of mixing a silicon compound to a solvent and kneading thermoplastics after the dissolution or distribution to it.

(30) The nonaqueous secondary battery which is at least one sort as which a paragraph (28) and the

¹Variables included in the model are chosen from previous studies that used multilevel regression analysis.

- (1) Paragraph (28) Nonaqueous secondary battery whose weight ratio of thermoplastic to the silicon compound of - (30) is 2 to 30%.

(32) Paragraph (28) Nonaqueous secondary battery whose coverage of the thermoplastics of - (31) is 5 to 95%.

(33) The nonaqueous secondary battery with which carbon lives together is to 1500% by a weight ratio to the silicon compound of a paragraph (1).

(34) The nonaqueous secondary battery with which carbon lives together 5 to 400% by a weight ratio to the silicon compound of a paragraph (1).

(35) The nonaqueous secondary battery a paragraph (33) and whose carbon of (34) are weakly natural graphite.

(36) The nonaqueous secondary battery whose ϵ is within the limits of 0 to 4.2 when the charge and discharge range of the silicon compound of a paragraph (1) expresses with Li_xSi to silicon as equivalent mass of the lithium which comes out insertion discharge.

(37) The nonaqueous secondary battery whose ϵ is within the limits of 0 to 3.7 when the charge-and-discharge range of the silicon compound of a paragraph (1) expresses with Li_xSi .

(38) The nonaqueous secondary battery which stopped charge of the silicon compound of a paragraph (3) in 0.1% or more of 1 hour rate current, and 10% or less of range.

(39) The nonaqueous secondary battery which charge given in a paragraph (38) ended within 10 hours 15 minutes or more.

(40) The positive active material of a paragraph (1) is Li_yMO_2 (1) [Mn/Co and] At least one sort of nickel, Fe, and Mn Nonaqueous secondary battery using at least one sort of the material containing $y=0.1-2$ or the material which has the Spinel structure expressed with $\text{Li}_y\text{N}_z\text{O}_4$ ($N=\text{Mn}/y=0.2$).

(41) The positive active material of a paragraph (1) is $\text{Li}_y\text{M}_z\text{D}_{1-y}\text{O}_2$ (1) [Mn/Co and] At least one sort of Nickel, Fe, and Mn, O=O₂, nickel, Fe, Mn, aluminum, Zn, Cu, Mo, Ag, W, Ga, In, Sn, Pb, Sb, Al, Inert unit and other than M in Sr, E, and P, $y=0.1-2$: the material containing $m=0.8-1$, or $\text{Li}_y(\text{N}_z\text{S}_{1-z})_2\text{O}_4$ (1) [2=Mn and] The nonaqueous secondary battery using at least one sort of material which has the Spinel structure expressed with at least one sort of Er₂O₃, nickel, Fe, aluminum, Zn, Cu, Mo, Ag, W, Ga, m, Sn, Pb, Sb, Sr, E, and P, $b=0.2-1$, and $z=0-2$.

(42) Paragraph (3) Nonaqueous secondary battery whose mean grain size of the silicon used by - (39) is 0.01-50 micrometers.

(43) Paragraph (3) Nonaqueous secondary battery whose mean grain size of the silicon used by - (38) is 0.05-5 micrometers.

(44) The nonaqueous secondary battery which is at least one sort by which silicon of a ultramicro is chosen as a paragraph (42) or (43) from the silicon single substance, silicon base alloy, and nitride which can react to lithium.

- (45) Paragraph (3) Nonaqueous secondary battery whose alloy given in - (11) is an alloy to which the cermet of paragraph (16) - (21) were made to adhere.
- (46) Paragraph (3) Nonaqueous secondary battery whose alloy given in - (11) is an alloy which covered the metal of paragraph (22) - (27).
- (47) The nonaqueous secondary battery whose alloy given in a paragraph (45) is an alloy which covered the metal of paragraph (22) - (27).
- (48) The nonaqueous secondary battery whose alloy given in a paragraph (46) is an alloy which covered the cermet of paragraph (16) - (21).
- (49) Paragraph (3) Nonaqueous secondary battery whose alloy given in - (11) is an alloy which covered the thermoplastics of paragraph (28) - (32).
- (50) The nonaqueous secondary battery which plated paragraph (22) - (27) into the material of the paragraph (46).
- (51) Paragraph (46) Nonaqueous secondary battery whose material of - (46) is the material which covered the thermoplastics of paragraph (28) - (32).
- (52) The nonaqueous secondary battery whose material of a paragraph (45) is the material which covered the metal of paragraph (28) paragraph (22) - (27) after covering the thermoplastics of - (32).
- (53) Paragraph (3) Nonaqueous secondary battery which is the material in which the alloy of the statement made carbon of paragraph (33) - (36) live together in - (11).
- (54) Paragraph (45) Nonaqueous secondary battery whose material given in - (52) is the material which made carbon of paragraph (33) - (36) live together.
- (55) Paragraph (3) Nonaqueous secondary battery which uses the negative electrode of a statement for - (11) in the charge-and-discharge range of a statement at paragraph (36) - (38).
- (56) Paragraph (35) Nonaqueous secondary battery which uses the material of a statement for - (54) in the charge-and-discharge range of a statement at paragraph (36) - (38).
- (57) An alloy given in a negative pole material of paragraph (3) - (11), the nonaqueous secondary battery using a compound given [as positive active material] in a paragraph (40) or (41).
- (58) The nonaqueous secondary battery using a compound given [as the material of paragraph (42) - (54), and positive active material] in a negative pole material a paragraph (40) or (41).
- (59) Paragraph (12) Nonaqueous secondary battery whose silicon given in - (15) is the silicon to which the cermet of paragraph (16) - (21) were made to adhere.
- (60) Paragraph (12) Nonaqueous secondary battery whose silicon given in - (15) is the silicon which covered the metal of paragraph (22) - (27).
- (61) The nonaqueous secondary battery whose material of a paragraph (59) is the material which covered the metal of paragraph (22) - (27).
- (62) The nonaqueous secondary battery whose material of a paragraph (60) is the material to which the cermet of paragraph (16) - (21) were made to adhere.
- (63) Paragraph (12) Nonaqueous secondary battery whose silicon given in - (15) is the silicon which covered the thermoplastics of paragraph (28) - (32).

- (64) The non-aqueous secondary battery which is the material which covered the metal of paragraph (22) - (27) and a material given in a paragraph (63).

(65) Paragraph (66) Nonaqueous secondary battery whose material of - (62) is the material which covered the thermoplastics of paragraph (28) - (32).

(66) The nonaqueous secondary battery whose material of a paragraph (67) is the material which covered the metal of paragraph (28) paragraph (22) - (27) after covering the thermoplastics of - (32).

(67) Paragraph (12) Nonaqueous secondary battery which is the material in which silicon of the statement made carbon of paragraph (33) - (36) live together in - (15).

(68) Paragraph (69) Nonaqueous secondary battery whose material given in - (66) is the material which made carbon of paragraph (30) - (36) live together.

(69) Paragraph (12) Nonaqueous secondary battery which uses the negative electrode of a statement for - (15) in the charge-and-discharge range of a statement at paragraph (36) - (39).

(70) Paragraph (68) Nonaqueous secondary battery which uses the material of a statement for - (69) in the charge-and-discharge range of a statement of paragraph (36) - (36).

(71) The nonaqueous secondary battery using a compound given [as silicon given in a negative pole material of paragraph (12) - (16), and positive active material] in a paragraph (40) or (41).

(72) The nonaqueous secondary battery using a compound given [as the material of paragraph (59) - (60), and positive active material] in a negative pole material a paragraph (40) or (41).

(73) Paragraph (16) Nonaqueous secondary battery which is the silicon in which the silicon compound of the statement covered the metal of paragraph (22) - (27) to - (21).

(74) Paragraph (16) Nonaqueous secondary battery whose silicon compound given in - (21) is a silicon compound which covered the thermoplastics of paragraph (28) - (32).

(75) The nonaqueous secondary battery whose material of a paragraph (73) is the material which covered the thermoplastics of paragraph (28) - (32).

(76) The nonaqueous secondary battery whose material given in a paragraph (75) is the material which covered the metal of paragraph (22) - (27).

(77) Paragraph (16) Nonaqueous secondary battery whose silicon compound given in - (21) is a silicon compound which made carbon of (32) - (36) live together.

(78) Paragraph (73) Nonaqueous secondary battery whose material given in - (77) is the material which made carbon of (32) - (36) live together.

(79) Paragraph (18) Nonaqueous secondary battery which used the silicon compound of the statement for - (21) with the charging and discharging method of the statement at paragraph (38) - (39).

(80) Paragraph (73) Nonaqueous secondary battery which used the material of the statement for - (75) with the charging and discharging method of the statement at paragraph (36) - (36).

(81) The nonaqueous secondary battery using a compound given [as a negative pole material / as the silicon compound of paragraph (16) - (21), and positive active material] in a paragraph (40) or (41).

- (82) The nonaqueous secondary battery using a compound given [as a negative pole material / as the material of paragraph (73) - (78), and positive active material] in a paragraph (40) or (41);
(83) Paragraph (22) Nonaqueous secondary battery which is the material to which the material of the statement made the chemicals of the statement adhere at - (27) of paragraph (16) - (21);
(84) Paragraph (23) Nonaqueous secondary battery whose material given in - (27) is the material which covered thermoplastics given in paragraph (26) - (32);
(85) The nonaqueous secondary battery which is the material in which the material of the paragraph (83) covered the thermoplastics of the statement to paragraph (28) - (32);
(86) Paragraph (24) Nonaqueous secondary battery whose material given in - (27) is the material which made carbon of paragraph (33) - (35) live together;
(87) Paragraph (85) Nonaqueous secondary battery whose material given in - (85) is the material which made carbon of paragraph (33) - (35) live together;
(88) Paragraph (25) Nonaqueous secondary battery whose material given in - (27) is the material which made carbon of paragraph (33) - (35) live together;
(89) Paragraph (26) Nonaqueous secondary battery which used the material of the statement for - (27) with the charging and discharging method of the statement at paragraph (36) - (37);
(90) Paragraph (86) Nonaqueous secondary battery which used the material of the statement for - (86) with the charging and discharging method of the statement of paragraph (36) - (38);
(91) The nonaqueous secondary battery using a compound given [as a material given / as a negative pole material / in paragraph (22) - (27), and positive active material] in a paragraph (40) or (41);
(92) The nonaqueous secondary battery using a compound given [as a material given / as a negative pole material / in paragraph (81) - (88), and positive active material] in a paragraph (40) or (41);
(93) Paragraph (16) Nonaqueous secondary battery whose material given in - (32) is the material to which the ceramics of (16) - (21) were made to adhere;
(94) Paragraph (28) Nonaqueous secondary battery whose material given in - (82) is the material which covered metal given in (22) - (27);
(95) The nonaqueous secondary battery whose material given in a paragraph (93) is the material which covered metal given in paragraph (22) - (27);
(96) Paragraph (29) Nonaqueous secondary battery whose material given in - (22) is the material which lived carbon of the statement together in paragraph (33) - (36);
(97) The nonaqueous secondary battery whose material given in a paragraph (93) is the material which lived carbon of the statement together at paragraph (33) - (35);
(98) The nonaqueous secondary battery whose material given in a paragraph (94) is the material which lived carbon of the statement together at paragraph (33) - (35);
(99) Paragraph (28) Nonaqueous secondary battery which used the material of the statement for - (27) with the charging and discharging method of the statement at paragraph (36) - (37);
(100) Paragraph (35) Nonaqueous secondary battery which uses the material of the statement for - (96) with the charging and discharging method of the statement of paragraph (36) - (38).

- (161) The nonaqueous secondary battery using a compound given [as a material given / as a negative pole material / in paragraph (38) - (32), and positive active material] in a paragraph (40) or (41)

(162) The nonaqueous secondary battery using a compound given [as a material given / as a negative pole material / in paragraph (50) - (58), and positive active material] in a paragraph (40) or (41).

(163) The nonaqueous secondary battery using a compound given [as a material given / as a negative pole material / in paragraph (33) - (36), and positive active material] in a paragraph (40) or (41).

(164) Paragraph (23): Nonaqueous secondary battery which used the material of the statement for (25) with the charging and discharging method of the statement of paragraph (38) - (39)

(165) Paragraph (62): Nonaqueous secondary battery which used the material of the statement for (44) with the charging and discharging method of the statement of paragraph (38) - (39)

[0008] On a charge collector, positive electrode mixture (or negative electrode mixture) can be painted and fabricated, and the anode (or negative electrode) used by this invention can make it. A conductive agent, a binder, a dispersing agent, a filler, an ion conducting agent and a pressure reinforcement agent, and various additive agents besides positive active material (or negative pole material) can be included in positive electrode mixture (or negative electrode mixture). As for these electrodes, it is preferred that they are discoid and a sheet shaped which is wavy although it may be tubular.

[0007] The composition and material of this invention are explained in full detail below. The compound containing the silicon atom which can carry out insertion discharge of the lithium used with the negative pole material of this invention means a silicon single substance, a silicon base alloy, and a silicate. A single crystal, polycrystal, and amorphous all can be used as a silicon compound. As for the purity of a single substance, 85 % of the weight or more is preferred, and its 90 % of the weight or more is especially preferred. Especially 99 % of the weight or more is preferred. As an impurity, Fe, aluminum, Ca, Mn, Mg, nickel, Cr, etc. are mainly contained. Those contents is 0 to 0.5 % of the weight. As for the mean grain size of a " silicon compound, 0.01-50 micrometers is preferred. In particular, 0.02-30 micrometers is preferred. 0.05-5 micrometers is preferred. Being covered with the silica dioxide is known well and the surface of silicon is considered to also carry out the duty of an ion conductivity coat.

[0010] Since a silicon base alloy controls the pulverization by expansion contraction of the silicon produced when insertion discharge of the lithium is carried out, or improves the conductive likeness of silicon, it is thought that it is effective. As an alloy, an alloy with alkaline-earth metals, a transition metal, or raremetal is preferred. In particular, a dissolution nature alloy and an eutectic nature alloy are preferred. A dissolution nature alloy says the alloy which forms a solid solution. For example, the alloy of gallium is a dissolution nature alloy. Although eutectic of the eutectic nature alloy is carried out to allow at any rate the solid cooled and obtained says the alloy which is a mixture of

silicon and metal. Be, Ag, aluminum, Au, Cd, Ga, In, Sn, Si, and Zn form an eutectic nature alloy. In these, the alloy of germanium, Be, Ag, aluminum, Au, Cd, Ga, In, Sn, Si, and Zn is still more preferred. Two or more sorts of these alloys are also preferred. The alloy which contains germanium, Ag, aluminum, Cd, In, Sn, Si, and Zn especially is preferred. As for the mixing ratio of these alloys, 5 to 95 % of the weight is preferred to silicon, in particular, 10 to 90 % of the weight is preferred. Especially 20 to 80 % of the weight is preferred. Other Mg of an inertial nature alloy, Fe, Cr, nickel, Ti, Mn, and W may also be included. As content of these metal, 0 to 20 % of the weight is preferred. The mixing ratio in particular of metal other than silicon is not limited. In this case, although electrical conductivity improves, it is preferred battery capacity and that specific conductance will be 10 or more times of silicon in front of an alloy or the specific conductance of a silicon compound in respect of service capacity, high rate characteristics, and a cycle life especially.

[0010]The calcining method and the mechanical milling method are used as a synthesis method of an alloy. In inactive gas, with the heating rate of 5-100 °C / min, as a calcining method, mix the mass of a raw material, move it to a crucible, carry out temperature up, and as constant temperature. Especially, preferably, it is kept especially desirable at 1300-1700 °C for 30 minutes - 5 hours for 10 minutes - 24 hours, and 1000-1800 °C cool with the above temperature falling speed by 10 °C. Cooling above by 100 °C especially is preferred. As inactive gas, it is preferred whether it is independent in gas, such as argon, nitrogen, and hydrogen, and that it mixes and uses. Annealing is performed after cooling. As an annealing condition, within the limits of the temperature which 200 °C, some alloys do not fuse is preferred in inactive gas.

[0011]The method of grinding two or more metal until it becomes finely detailed is used, using grinders, such as a ball mill, a planetary ball mill, and a vibration mill, as a mechanical milling method. As for the inside of the cell of a mill, it is preferred to fill with inactive gas, an inert liquid object, a reducing gas, and a reducing fluid. As inactive gas, it is preferred whether it is independent in gas, such as argon, nitrogen, and hydrogen, and that it mixes and uses. Water, alcohol, etc. when ****ed are used as an inert liquid object. Ammonia, sulfuric acid gas, etc. are used as a reducing gas. As a reducing fluid, acetone and the dimethylsulfide solution having contained scandium sulfate, sodium sulfite, hydroxymamine, hydroquinone, etc. can be used. Especially the thing that inactive gas grinds is preferred. As for milling time, 1 hour - 48 hours are preferred.

[0012]As for the mean grain size of an alloy 0.01-10 micrometers is preferred. 0.02-20 micrometers is preferred especially, and especially further 0.03-5 micrometers are preferred. As the grinding method, a vibration mill, a ball mill, a planetary ball mill, a jet mill, and an automatic molar are used. As for grinding time, 1 minute - 1 hour are preferred. The method which stated the atmosphere of grinding by the paragraph of mechanical milling is used.

[0013]A electrode says the compound of silicon and metal. As a silicide, CaSi₂, Mg₂Si, BaSi₂, SrSi₂, Cu₂Si, Fe₂Si, FeSi₂, CuSi₂, nickel₂Si, NiSi₂, MnSi₂, MoSi₂, CrSi₂, TiSi₂, Ti₂Si, Cr₂Si, Ni₂Si₂, NiSi₂, CeSi₂, SmSi₂, DySi₂, ZrSi₂, WSi₂, W₂Si₃, TaSi₂, Ta₂Si₃, TmSi₂, TbSi₂, YbSi₂, YSi₂.

YS_2 , Er_2Si_2 , CaSi_2 , PMS , V_2S_3 , VS_2 , MgSi_2 , PdSi , PrSi_2 , HoSi_2 , EuSi_2 , LaSi_2 , PdSi_2 , ReSi_2 , NbSi_2 , etc. are used.

[081] It is preferred to use the silicon which removed metal from the metal silicide as the silicon compound. When the porous thing and the fine grain condensed by a particle of 1 micrometer or less in shape of this silicon, and formed the porous aggregated particle can be raised. It is thought as a reason; a cyclic life will be improved if the silicon is used that pulverization is hard to be carried out. As for the metal of the metal silicide, it is preferred that they are an alkaline metal and alkaline-earth metals. Especially, it is preferred than they are Li, Ca, and Mg. In particular, Li is preferred. As for the mean grain size of the metal silicide, it is preferred that it is 0.01-300 micrometers, its 0.01-50 micrometers are more preferred, and its 0.01-10 micrometers are the most preferred. 100-420-mol% of the lithium content of this lithium silicide is desirable to silicon. In particular, 200-420-mol% is preferred. As for the method of removing an alkaline metal and alkaline-earth metals from the silicide of an alkaline metal or alkaline-earth metals, it is preferred to make it process with the solvent related to an alkaline metal or alkaline-earth metals. As a solvent, water and alcohol are preferred, *** in which using the alcohol which dissolved in the case of the lithium silicide, and were dried can further oxidation of silicon under reaction is preferred. As a grade of drying, 1000 rpm or less of residual amount of water is preferred, 200 rpm or less are preferred, and 50 rpm or less are the most preferred. As the method of desorption and drying, carrying out bubbling with inactive gas, such as argon, is mentioned, making the alcohol return. As a kind of alcohol, methyl alcohol, ethyl alcohol, 1-propyl alcohol, 2-propyl alcohol, 1-butyl alcohol, 2-butyl alcohol, 1-pentyl alcohol, 2-pentyl alcohol, and 3-pentyl alcohol are preferred. In particular, 1-propyl alcohol, 2-propyl alcohol, 1-butyl alcohol, 2-butyl alcohol, and 3-butyl alcohol are preferred. Removal of Ca or Mg has preferred water. It is still more desirable when a buffer for pH which is maintained at neutral vicinity is used. Especially although after is necessary is just more than the reaction equivalent as an amount of solvents, about 10 times are preferred. Although reaction temperature does not have restriction in particular, in order to advance a reaction mildly and uniformly it is preferred that it is below a room temperature.

[084] Coating is preferred after taking out the resultant silicon powder after ending reaction by filtration or a decantation. As a penetrant remover, the above-mentioned water and alcohols are preferred. Thus, as for the integral shape of the obtained powder, it is preferred that it is 1 or less % of the weight, and it is more preferred that it is 0.1 or less % of the weight, in order to lessen wear usage, it is preferred to make grain size of the silicide of reaction time small. Specifically 0.01-200 micrometers is preferred, 0.01-50 micrometers is more preferred, and 0.01-10 micrometers is the most preferred. After grinding the powder obtained after ending reaction as other methods and making grain size larger, subjecting to a resultant solvent again is also preferred. It is also preferred to repeat the aforementioned grinding and a reaction if needed. True, it is preferred that the after-mentioned causes off metallic coating of the obtained silicon powder at the point that service capacity and a cyclic life are further improvable.

[0015] It is thought that the ceramics made to adhere to a silicon compound are effective in control of the pulverization of silicon. The compound which does not react to silicon in principle as ceramics is preferred. In particular, aluminum₂O₃, SiO₂, TiO₂, SiC, and Si₃N₄ are preferred. As a method in which silicon and ceramics are made to adhere, although melting, heating, vacuum evaporation, and CVD are used, powder-dilution use of mixing and heating is preferred especially. After carrying out dispersion mixing of the colloidal solution (colloidal silicon and silicon of aluminum₂O₃ or SiO₂, especially, it can heat, the lump which dissolved can be ground and the alloy of silicon, aluminum₂O₃ or SiO₂ can be obtained. With in this case, the alloy of aluminum₂O₃ or SiO₂. The state where the surfaces, such as aluminum₂O₃ and SiO₂, are covered with silicon powder, is set up inside lumps, such as aluminum₂O₃ and SiO₂, or they are covered for the surface of silicon is used. Mechanical agitation, an ultrasonic wave, and kneading can attain mixture dispersion. Although it is preferred to perform heating in 300 °C - 1000 °C in inactive gas, 500 °C - especially 1000 °C especially are still more preferred 400 °C - 1000 °C. Cooking time's 0.5 to 24 hours are preferred. As for inactive gas, argon, nitrogen, and hydrogen are used. These inert gas is also used. The method which was treated with a ball mill, the vibration mill, the planetary ball mill, the jet mill, the sufficient autogenous miller, etc. as for pulverizing method is used. Although the environment which also stated this grinding by mechanical milling is preferred, it is preferred to be especially carried out in inactive gas. Although the mixture ratio of the ceramics to silicon has 2 to 50% of the weight of a preferred range, 3 to 40% is especially preferred. As for the mean grain size for which it asked from electron microscopy observation of silicon, 0.01-40 micrometers is preferred, 0.5-20 micrometers is preferred especially, and 1-10 micrometers is still more preferred.

[0016] As metallic coating of the silicon compound of this invention, it can attain by vacuum deposition, such as electroplating, the substitution plating method, a non-electrolytic plating method, resistance heating vacuum deposition, electron beam evaporation, and cluster ion vacuum deposition, sputtering process, and a chemical-vapor-deposition method (CVD method). In particular, vacuum deposition, such as a non-electrolytic plating method, resistance heating vacuum deposition, electron beam evaporation, and cluster ion vacuum deposition, sputtering process, and a CVD method are preferred. The method of pushing thin metal by the high-speed-shearing mill, the stamp mill, and a roll mill is used. Especially, especially a non-electrolytic plating method is preferred. A non-electrolytic plating method is a volume for "non-electrolytic plating formulation and application" structuring study groups. ***** (1994) It is indicated. The reducing agent has ascorbate, phosphite, boron hydride ghet, aldehyde, sugar, amine, and preferred metal salt. Sodium hydrogen orthophosphate and sodium hydrogen metaphosphate, sodium borohydride, dimethylamine borane, formaldehyde, sucrose, dextin, hydroxylamine, hydrazine, ascorbic acid, and a barium chloride are preferred. It is preferred to include a pH regulator and complexing agent other than a reducing agent in plating liquid. The compound indicated above "the non-electrolytic plating formulation and application" also show there is used. The plating solution presentation is also

described in the above-mentioned book. As for the concentration of a reducing agent, over 1 (10-50%) g/l of water are preferred. Although the pH in particular of plating liquid is not limited, 4-12 are preferred although 10 ** - 100 ** are preferred as for the temperature of liquid - especially -- 20 ** - 90 ** - this - however - **. The activation bath which consists of a SnCl_4 hydrochloric acid aqueous solution besides a plating bath, and the nucleation bath which consists of a PdCl_2 hydrochloric acid aqueous solution; or a filtering step, a washing process, a grinding process and a drying process are used further.

(0017)Moreover -- on the part of the silicon compound covered -- with powder state mass tabular, etc. -- although -- it is used, if the metal covered is conductive high metal, it is ; anything I good, but nickel, Cu, Ag, Co, Fe, Cr, W, Ti, Au, Pt, Pd, Sn, and Zn are preferred especially, nickel, Cu, Ag, Co, Fe, Cr, Au, Pt, Pd, Sn, and Zn are preferred especially, and nickel, Cu, Ag, Pt, Sn, and especially Zn are still more preferred. Although the amount of metal in particulate covered does not have limitation, it is preferred to cover so that specific conductivity may be 10 or more times of the specific conductivity of the silicon compound which is a base. As for especially metalized coating volume, 1 to 10 % of the weight is preferred one to 80% of the weight to silicon, and especially its further 1 to 90% of the weight is preferred.

(0018)As for the silicon compound used by this invention, being beforehand covered with the synthetic resin selectively is preferred from a viewpoint of improvement of a cycle life. It is thought that it is because the pulverization of the silicon compound accompanying lithium insertion is controlled as a reason a cycle life is improved. Although a synthetic resin is divided roughly into thermoplastic and thermosetting resin, for cycle-life improvement, thermoplastics is more preferred. As for thermoplastics, a fluorine-containing high molecular compound, imide system polymers, vinyl system polymers, acrylate system polymers, ester system polymers, polysiloxane, etc. are used especially thermoplastics has preferred resin which cannot swell easily to an electrolysis solution. As an example, polyacrylic acid, polyacrylic acid Na, polyvinyl phenol, Polyvinyl methyl ether, polyvinyl phenol, a polyvinyl pyrrolidone, Water-soluble polymer, such as polyacrylamide, polyhydroxy(meth)acrylate, and a styrene-maleic acid copolymer, Fluorovinyl chloride, polytetra(FURUFO)ethylene, polyvinylidene fluoride, A tetrafluoroethylene-hexafluoropropylene copolymer, a vinylidene fluoride-tetrafluromethylene-hexafluoropropylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), Sulfonation EPDM, polyvinyl-acetate resin, a methylmethacrylate, The acrylic ester copolymer containing acrylic ester (methyl), such as 2-ethylhexyl acrylate (methyl).

(0019)The polyvinyl ester copolymer containing vinyl ester, such as an acrylic acid ester acrylonitrile copolymer and vinyl acetate, A styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer, polybutadiene, neoprene rubber, Fluorocarbon rubber, polyethylene oxide, polyester polyurethane resin, An emulsion (staled or suspension, such as polymer polyurethane resin, polycarbonate polyether(ene) resin, polyester resin, phenol resin, and an epoxy resin), can be mentioned. Links of a polyacrylic ester system, carboxymethyl cellulose, polyvinylfluoridethylene, and polyvinylidene fluoride are mentioned especially. It can be independent or it can mix and these compound can be used in

it is a solvent which can dissolve a synthetic resin as a solvent used here, anything can be used but in the case of polyvinylidene fluoride, N-methyl-2-pyrrolidone or dimethylformamide is preferred. After dissolving thermoplastics in an option covered beforehand by carrying out homogeneous mixing after mixing of synthetic resin powder and the silicon compound powder, the method of getting the obtained solid is also preferred. When grinding the obtained solid, it is preferred to grind under the inert gas atmosphere of argon, etc. for control of side reactions, such as oxidation of a silicon compound. Generally the directions as a binder at the time of the thermoplastic is shown above insulating a negative electrode mixture layer are known. The directions as cooling of this invention differ in that an active material surface is made to carry out localization of the thermoplastic to the directions as a binder using the methods of mixing with an active material, a conducting agent, etc uniformly, and using. Although it is known conventionally that it is a direction from which a cycle life is improved by increasing the amount of the thermoplastic used as a binder, the method of the cycle nature improvement effect which the active material surface of this invention is made to cover is larger.

[0019] As amount of the synthetic resin used in a silicon compound, 2 to 30 % of the weight is preferred; in particular, 3 to 20 % of the weight is preferred. As for a synthetic resin, in the invention, being covered selectively is preferred. Although 5 to 95% of coverage is desirable, 5 to 90% is preferred especially. It defines as the rate of percentage of the area of the portion covered with the thermoplastic to the total surface area of silicon compound particles with coverage here. Since it is generally insulation, when covering thermoplastics on the silicon compound surface, it is preferred to use together the means which raises conductivity. As a means which raises conductivity, publicly known methods, such as coexistence with carbon particles, coexisting with metal particles, and concurrent use of metal plating, can be used. As for the average size of the covered particles, 0.01 micrometer - 40 micrometers are preferred. In particular, 0.03-5 micrometers is preferred. It is preferred to use the carrier fluid which a synthetic resin does not dissolve as carrier fluid used when mixing with a conducting agent and a binder the particles covered with the synthetic resin, and preparing negative electrode mixture. For example, when it covers with polyvinylidene fluoride, the carrier fluid used at the time of negative electrode mixture preparation has preferred water. The method of the above [the grinding method or its environment] is used, it is preferred to use metalized cooling together because of grant of electron conductivity.

[0020] It is preferred to mix and use a silicon compound and a carbonaceous compound in this invention. The material for which a carbonaceous material is used with a conducting agent or a negative pole material is used. As a carbonaceous material, the charge of a difficulty graphitized carbon material and a black lead system carbon material can be mentioned. Specifically JP, 62-

these compounds, a fluorine-containing high molecular compound is preferred.

Polytetrafluoroethylene and polyvinylidene fluoride are especially preferred. As a method of covering, beforehand, a synthetic resin sheet is dissolved or dispersed, and a silicon compound is mixed and kneaded in the solution. The method of grinding the solid obtained by drying the solution is preferred.

122095 A, JP 2-64966 A. The spacing indicated in each gazette, such as 3-265473, density, the carbon material of the size of microcrystal, the mixture of natural graphite and an artificial graphite powder in JP 5-290644 A, JP 63-24585 A, 63-13282, 43-58763. They are a vapor-phase-epoxy carbon material given in JP 6-212617 A, and the material by which heating calcination was carried out at the temperature over 2400 °C in difficulty graphitized carbon given in JP 5-162666 A. And materials with the peak of the X-ray diffraction equivalent to two or more 90 and page, JP 5-307507 A, 5-207658, 7-95662, the meso face carbon material compounded by the 8-318220 gazette by non-calcination of the statement. To black lead and the part which have an overwaxing layer of a statement in JP 8-84516 A. Carbon materials, such as poly acene material containing the taking body of various kinds of granules, a microsphere, a plate-like object, microfilament, the carbon material of the shape of a whisker, phenol resin, acrylonitrile resin, and furfuryl alcohol resin and a hydrogen atom, etc., can be mentioned. As an example as a conducting agent, natural graphite such as flaky graphite, sooty graphite, and earthy graphite, High-temperature-burn objects, such as petroleum coke, coal coke, cellulose, sugars, and a mesophase pitch. Graphite, such as artificial graphite, such as vapor-phase-epoxy black lead, acetylene black, Carbon materials, such as carbon black, such as furnace black, Ketjen black, channel black, lamp black, and thermal black, an asphalt pitch, coal tar, activated carbon, a meso fuz pitch, and poly acene, are preferred. These may be used independently and may be used as a mixture.

In particular, the baking body of a carbon material given in JP 5-182464,A, various kinds of granules, a microsphere, a plate-like object, textiles, the carbon material of the shape of a wicker and a mesophase pitch, phenol resin, and acrylonitrile resin and the poly aromatic material which contains a hydrogen atom further are preferred. Only natural graphite especially - a medium - it is desirable in order to strengthen a film. 5 to 1800 % of the weight of the mixture ratio is preferred to a silicon compound. In particular, 20 to 150 % of the weight is preferred, 30 to 400 % of the weight is preferred. Although various things can be used as a mean grain size of a carbureaceous material, 0.01-0.1 micrometers is preferred, 0.02-30 micrometers is more preferred, and 0.03-5 micrometers is the most preferred.

[0022] As a conducting agent, other carbonaceous materials can be used as follows. When the ratio of the lithium which can carry out insertion discharge to a silicon atom is expressed with Li/Si as a charge-and-discharge range of a silicon compound negative pole material, $\gamma = 0.4-2$ is preferred. As a result of considering cycle-life improvement of silicon wholeheartedly, when stopped in the range of $\gamma = 0.3-1$, the cycle life found out improving greatly. In $\gamma = 3/7$, it was about 0.95C to being [an upped to i at charging potential] a lithium metal counter electrode 1.0 V in $\gamma = 4/2$ including average voltage as updated to the shape of a discharge curve changing and a discharge curve flat to the 0.5V [body lithium metal] neighborhood in a 0.0V charge circuit being obtained at the time. -- more than 1.05V -- especially -- more than 0.48V ($\gamma = 3/8$) -- start -- the gently sloping curve which has average voltage in 0.4V is obtained. This is, the duration when increased charge beginning-and-the-end voltage round out the specific rate increase in which discharge voltage fall. The enhancement which the

reversibility of the charge and discharge reaction also went up was found out.

[0023] As the charge beginning-and-the-end method in this invention, although methods, such as combination of an open circuit constant voltage, a closed circuit constant voltage, current, time, and the same current charge after high current charge, are used, the method of setting up and doubling the current at the time of a closed circuit constant voltage, and setting up charging time especially, is preferred. A constant voltage value is set up in a mentioned range. As far as a current value, it is preferred to stop charge when it goes into 0.1 to 110% of range of 1 hour rate current in a constant voltage form.

[0024] Although the method with the effect of improving a cycle life had been described separately, maintaining the high capacity of a silicon compound, the cell more desirable made found out by using the still higher improvement effect with the combination of a described method.

[0025] In this invention, it is combinable with the compound which can carry out insertion discharge of the lithium, such as the other carbonaceous materials or the silicon compound of this invention, an oxide material, a nitride material, sulfide material, a lithium metal, and a lithium alloy, as a negative pole material. Especially when using a transition metal oxide for a positive electrode material, it uses together with a lithium metal or a lithium alloy.

[0026] The positive electrode material used by this invention has an especially preferred lithium containing transition metal oxide, although the transition metal oxide in which the insertion discharge of the lithium can be carried out is used. It is an oxide which mainly contains preferably Ti, V, Cr, Mn, Fe, Co, nickel, Mo, at least one sort of transition metal elements chosen from V, and lithium, and the mole ratio of lithium and a transition metal is a compound of 0.3 through 2.2. It is an oxide which mainly contains more preferably at least one sort of transition metal elements chosen from V, Cr, Mn, Fe, Co, and nickel, and lithium, and the mole ratio of lithium and a transition metal is a compound of 0.1 through 2.2; aluminum, Ga, or, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. may be contained in less than 30 mole percents to the transition metal which mainly exists. In the above-mentioned positive active material, it is general formula $\text{Li}_x\text{MO}_y\text{O}_z$ (O; M=Co and J at least one sort of nickel, Fe, and Mn using at least one sort of material which has the Spinel structure expressed with $x=0.1-2$ or $1 \leq y \leq 2$, O; M=Co and J at least one sort of nickel, Fe, and Mn using at least one sort of material which has the Spinel structure expressed with $x=0.1-2$ or $1 \leq y \leq 2$ -- this -- better -- " Specifically Li_xCoO_2 , Li_xMnO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_y\text{nickel}_{2-y}\text{O}_2$, $\text{Li}_x\text{Co}_y\text{V}_{2-y}\text{O}_2$, $\text{Li}_x\text{Co}_y\text{Fe}_{2-y}\text{O}_2$, $\text{Li}_x\text{Mn}_y\text{O}_2$, $\text{Li}_x\text{Mn}_y\text{Co}_{2-y}\text{O}_2$, $\text{Li}_x\text{Mn}_y\text{nickel}_{2-y}\text{O}_2$, $\text{Li}_x\text{Mn}_y\text{V}_{2-y}\text{O}_2$, it is $\text{Li}_x\text{Mn}_y\text{Fe}_{2-y}\text{O}_2$ (it is x=0.02-1.2, an 0.1 to 0.9, b=0.6 to 0.98, c=1.6-1.86, and z=2.01-2.3 here).

[0027] Positive active material is $\text{Li}_y\text{M}_z\text{D}_{1-z}\text{O}_2$ (M=Co and J) At least one sort of nickel, Fe, and Mn using at least one sort of nickel, Fe, Mn, aluminum, Zn, Cu, Mo, Ag, W, Ga, In, Sn, Pb, Sb, At least one sort other than Mn in Sb, B, and P y=0.1-2, material containing an 0.5-1, Or $\text{Li}_y(\text{N}_x\text{E}_{1-x})_z\text{O}_2$ (N=Mn, Er, Co and J) nickel, Fe, Ga, aluminum, Zn, Cu, Mn, Ag, W, Ga, In, Sn, Pb, Sb, Si, B, and P-E have especially a preferred thing in which at least one sort of material which has the Spinel structure expressed with 1 sort b=1.0-2 z=0-2 at least is used. As more desirable lithium containing transition metal oxide,

Li_xCoO_y , Li_xMnO_y , Li_xMnO_2 , Li_xCoO_2 nickel_xO_y, $\text{Li}_x\text{Mn}_{1-y}\text{O}_y$ and $\text{Li}_x\text{Co}_{1-y}\text{V}_{1-y}\text{O}_y$ (x: 0.02-1.2, y: 0.1 to 0.9, y: 0.9 to 0.95, x: 0.01-2.2) are raised. The value of x is a value before a charge-and-discharge start, and is fluctuated by charge and discharge. Although the positive active material used by this invention is compounded by the method and solution reaction which mix a lithium compound and a transition metal compound and are calcinated especially its calcination method is preferred. The details for calcination are indicated in the paragraph 35 of JP-B-60-867,A, JP 7-14 578 A, etc., and these methods can be used for them. The positive active material obtained by calcination may be used after water, aqueous acidic, an alkaline aqueous solution, and an organic solvent wash. It may be the method of compounding by mixing a transition metal oxide related to a lithium metal, a lithium alloy, basic lithium, and a transition metal oxide as a method of inserting a lithium ion chemically.

[0038] Although the mean grain size in particular of the positive active material used by the invention is not limited, 0.1-50 micrometers is preferred. It is preferred that the volume of a 0.5-50-micrometer particle is not less than 95%, it is still more preferred that the volume which a particle group with a particle diameter of 9 micrometers or less occupies is 15% or less of whole products, and the volume which not less than 15-micrometer a particle group of 25 micrometers or less occupies is 18% or less of whole products. Although not limited especially as specific, surface area, $0.01-50\text{-m}^2/\text{g}$ is especially preferred as a BET adsorption method, and $0.2\text{-m}^2/\text{g}$ is preferred. As the pH of supernatant liquid when the positive active material 5g is melted in 100 ml of distilled water, 12 or less [7 or more] are preferred.

[0029] When obtaining the positive active material of this invention by calcination, it is 700-1200 °C that is 800-1500 °C as calcination temperature desirable still more preferably, and it is 750-1000 °C especially preferably. As firing time, 4 to 30 hours is 6 to 20 hours desirable still more preferably, and it is 8 to 15 hours especially preferably.

[0030] If the conductive agent used for the mixture of this invention is a carbon unburnable material which does not cause a chemical change in the constituted cell, it is [] anything good. As an example, natural graphite, such as flaky graphite,鳞状石墨, and sandy graphite, petroleum coke, High-temperature-burning objects, such as coal cokes, cellulose, sugars, and a mesophase pitch, Graphite, such as artificial graphites, such as vapor-phase-epoxy black lead, acrylonitrile black, Furnace black, Kitchen black, charcoal black, lamp black, Carbon black, such as thermal black, an asphalt pitch, coal tar, Conductive metallic oxide, such as conductive whiskers, such as metal powders, such as conductive fibers, such as carbon materials, such as activated carbon, a metal fiber which, and polyacrylate, and a metal fiber, copper, nickel, aluminum, and silver, a zinc oxide, and barium titanate, and barium oxide, etc. can be mentioned, it is desirable when an aspect ratio above five or more plate-like things in black lead, In these, graphite and carbon black are preferred, as for the size of particles, 6.04 micrometers or more and 20 micrometers or less are preferred, and its particle (0.02 micrometers or more and 10 micrometers or less) is more preferred. These may be mixed independently and may use two or more sorts together. It is desirable when using together, and 1-15-micrometer graphite-grain size is used together with carbon black, such as acrylonitrile black.

As for the addition to the binder layer of a conducting agent, it is preferred that it is 1 to 50 % of the weight to a negative pole material or a positive electrode material, and it is especially preferred that it is 2 to 30 % of the weight. In carbon black or graphite, it is preferred that it is especially 2 to 20 % of the weight.

[0031] In the invention, in order to hold an electrode compound, a binder is used. As an example of a binder, the polymer etc. which have polysaccharide, thermoplastic, and rubber elasticity are mentioned. As a desirable binder, starch, carboxymethyl cellulose, Cellulose, diethyl cellulose, methyl cellulose, hydroxyethyl cellulose, Hydroxypropylcellulose, alginate, acid Na, polyacrylic acid, Polyacrylic acid Na, polyvinyl phenol, polyvinyl methyl ether, Polyvinyl alcohol, a polyvinyl pyrrolidone, polyacrylamide. Water-unable polymer, such as poly-hydroxy (methyl) acrylate and a styrene-maleic acid copolymer, Polyvinylchloride, polyurethane FURURORD ethylene, polyvinylidene fluoride. A tetrafluoroethylene-hexafluoropropylene copolymer, a vinylidene fluoride tetrafluoroethylene-hexafluoropropylene copolymer, Polyethylene, polypropylene, an ethylene-propylene diene terpolymer (EPDM), The acrylic ester copolymer (maleic, acrylic acid (meth) ester acrylonitrile copolymer containing acrylic ester (maleic), such as sulfonation EPDM, polyvinyl-acetal resin, a methacrylate, and Z-ethylhexyl acetate, The polyvinyl ester copolymer containing vinyl ester, such as vinyl acetate, A styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer, Polybutadiene, neoprene rubber, fluorocarbon rubber, polyethylene oxide, An emulsion (latex) or suspension, such as polyester polyurethane resin, polyether polyurethane resin, polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxide resin, can be mentioned. Latex of a polyacrylic ester system, carboxymethyl cellulose, polytetrafluoroethylene, and polyvinylidene fluoride are mentioned especially. As for these binders, it is preferred to use when distributed minute powder in water, it is more preferred to use that whose average size of the particles in dispersion liquid is 0.01-5 micrometers, and it is preferred especially to use what is 0.05-1 micrometer, it can be independent, or it can mix and these binders can be used. When there are few additions of a binder the holding power and cohesive force of an electrode compound are weak. If too large, an electrode body product will increase and electrode unit volume or the capacity per unit weight will decrease. As for the addition of a binder, 1 to 30 % of the weight is preferred for such a reason, and 2 to 10 % of the weight is especially preferred.

[0032] In the constituted cell, a bulking agent can be used anything, if it is the fibrous material which does not cause a chemical change. Usually, textiles, such as olefin system polymer, such as polypropylene and polyethylene, glass, and carbon, are used. Although the addition in particular of a fiber is not limited, 0 to 30 % of the weight is preferred. The thing known as an inorganic and organic solid electrolyte can be used for an ion-conducting agent, and it is indicated in the paragraph of the electrolyte solution for details. A pressure enhancement agent is a compound which increases the internal pressure of a cell, and carbonates, such as Na_2CO_3 , is examples of representation.

[0033] The species of the charge collector which can be used by this invention are aluminum, stainless steel, nickel, titanium- or these alloys, and negative electrodes are copper, stainless steel, nickel,

silverum, or the like alloys. The peatall of a charge collector is foil, an expanded metal, a puncturing metal, or a wire gauze. In particular, to an anode, copper foil is ; aluminum foil and a negative electrode ; preferred. As thickness of foil, 7 micrometers - 100 micrometers are 7 micrometers - 50 micrometers desirable still more preferably, and they are 7 micrometers - 20 micrometers especially preferably. As thickness of an expanded metal, a puncturing metal, and a wire gauze, 7 micrometers - 200 micrometers are 7 micrometers - 150 micrometers desirable still more preferably, and they are 7 micrometers - 100 micrometers especially preferably. As purity of a charge collector, not less than 90% is not less than 98% desirable still more preferably, and it not less than 99.9% especially preferably. Acet, alkali, an organic solvent, etc. may wash the surface of a charge collector.

[0034]The thing of a charge collector in which the metal layer was formed on both sides of a plastic sheet is still more preferred in order to make thickness thin. The thing of a plastic excellent in durability and heat resistance is preferred, for example, it is polyethylene terephthalate. Only with metal since there is almost no elasticity, it is weak to external force. If a metal layer is formed on a plastic, it will become strong against a shock. More specifically, a charge collector may be a compound charge collector which covered substrate, such as a synthetic resin film and paper, with the substance of electron conductivity. As a synthetic resin film used as a substrate, a butyrate, polyethylene terephthalate, polycarbonate, polycarbonate, polyvinyl chloride, polystyrene, polyethylene, polypropylene, polyimide, polyamide, a cellulose dielectric, and polycarbonate can be mentioned. As a substance of the electron conductivity which covers a substrate, metallic elements and their alloys, such as carbonaceous materials, such as black lead and carbon black, aluminum, copper, nickel, chromium, iron, molybdenum, gold, and silver, can be mentioned. Especially the substance of desirable electron conductivity is metal, and are aluminum, copper, nickel, and stainless steel. A compound charge collector may be a gelatin which pastes the sheet and metal sheet of a substrate together, and may form a metal layer by vacuum evaporation etc.

[0035]Next, the composition of the positive-negative electrode in the invention is explained. As far as positive-negative electrode, it is preferred that it is the gelatin which applied the electrolytic compound to both sides of a charge collector. In this case even if the number of layers per one side is one layer, if they comprise more than two-layer. When the number of the layers per one side is two or more, a positive-active-material (or negative-pole material) contained layer may be more than two-layer. More desirable composition is a case where it comprises a layer containing positive active material (or negative-pole material), and a layer which does not contain positive active material (or negative-pole material). The protective layer for protecting the layer containing positive active material (or negative-pole material). The interlayer between the divided positive-active-material (or negative-pole material) contained layers, the under coat between a positive-active-material (or negative-pole material) contained layer and a charge collector, etc. are, and these are named generically in this invention and it is called an auxiliary layer.

[0036]As for a protective layer, it is preferred that it is in either both positive-negative electrodes or a

positive/negative electrode. In a negative electrode, as for a negative electrode, when it is being placed in a negative pole material within a cell, it is desirable that it be a gelatil which has a protective layer. A protective layer consists of at least one layer, and may be constituted by one or two or more layers of a different kind. It may be a gelatil which has a protective layer only on one side of the binder layers of both sides of a charge collector. These protective layers comprise particles, a binder and insoluble in water nature. The binder used when forming the above-mentioned electrode compound can be used for a binder. As particles of insoluble in water nature, a various conductive particle and the organic and inorganic particles which do not have conductivity substantially can be used. 100 PPM or less, and the desirable insoluble thing of the solubility to the water of insoluble in water nature particles are preferred. As for the rate of the particles contained in a protective layer, 2 S % of the weight or more and 90 % of the weight or less are preferred. It is more preferred, and is preferred, [of 10 % of the weight or more and especially 93 % of the weight or less] ; of 5 % of the weight or more and 90 % of the weight or less] .

[037] As a conductive particle of insoluble in water nature, carbon particles, such as metal, a metallic oxide, a metal fiber, carbon fiber, carbon black, and black lead, can be mentioned. In these water-insoluble conductive particles, what has low reactivity with an alkaline metal, especially lithium is preferred, and metal powder and a carbon particle are more preferred. An electrical resistivity of $20\text{ }\mu\Omega\cdot\text{cm}$ or less of the element which constitutes particles, below $50\text{ }\mu\Omega\cdot\text{cm}$ is preferred.

100398As metal powder, metal with low reactivity with lithium, i.e., the metal which cannot make a lithium alloy easily, is preferred, and, specifically, copper, nickel, iron, chromium, molybdenum, titanium, tungsten, and tantalum are preferred. A needle and a column, tubular, and massive may also be sufficient as the form of such metal powder, 0.02 micrometers or more and 20 micrometers or less have a preferred overall diameter, and 2 is more preferred [or 0.1 micrometers or more and 10 micrometers or less] that [the] in which the surface has not oxidized too much is preferred, and as for such metal powder, when having oxidized, heat-treating by reducing atmosphere is preferred.

The conductive agent used when an electrode active material is not conductively conventional can be used. The conducting agent used when specifically making an electrode compound is used.

(0.04%) are insoluble in water nature particles which do not have conductivity substantially. The incombustible powder of Teflon, SiC, aluminum nitride, alumina, zirconia, magnesia, mullite, boroncarbide, and a steatite can be mentioned. When these particles may be used together with a conductive particle and used by 0.01 or more times of a conductive particle, and 10 or less times, they are referred.

(b)(4) A positive (negative) electrode sheet can be created by applying, drying and compressing the mixture of a right (negative) pole on a charge collector. Preparation of a mixture mixes positive active material (or negative pole material) and a conducting agent. A binder (the suspension of resin powder) encloses-like thing; and carrier fluid can be added; kneading mixing can be carried out, and it can partly not suffice-entirely by stirring mixer, such as a mixer, a homogenizer, disperser, a planetary

shaker, a paint shaker, and a sand mill, and a dispersion machine distributing water is preferred although water or an organic solvent is used as carrier fluid. In addition, additive agents, such as a bulking agent, an ion conducting agent, and a moisture enhancement agent, may be added suitably. As for the pH of dispersion liquid, in a negative electrode 7-10 are preferred at 5-10, and no above [0042]Although spreading can be performed by various methods, the reverse roll method, the Delashew method, the braid method, the knife method, the extrusion method, a silicon agglomeration test, the curtain method, the photogravure method, the bar method, a dry method, and the squeeze method can be mentioned, for example. The method of using an extrusion die, and especially the method of using a blade coating machine are preferred. As for spreading, it is preferred to carry out the speed is 0.1-100 mm. Under the present circumstances, according to the liquid nature of mixture paste, and drying property, the surface state of a good coating layer can be acquired by selecting the above-mentioned coating method. It is preferred from viewpoints of manufacture of a uniform electrode, a manufacturing cost, etc. to apply two or more of those layers simultaneously, when electrode layers are two or more layers. The thickness, length, and width of the coating layer are decided with the size of a cell. The thickness of a typical coating layer is 10-1000 micrometers in the state where it was compressed after desiccation. The electrode sheet after spreading is dried and dried by the hot wind, a vacuum, infrared rays, far-infrared rays, an electron beam, and the operation of the damp way. These methods can be independent, or can be combined and can be used. The range of drying temperature of 80-150 °C is preferred, and its range which is 100-250 °C is especially preferred. As for the water content after desiccation, 2000 ppm or less are preferred, and its 500 ppm or less are more preferred. Although the compression of an electrode sheet can use the pressing method generally adopted, a die-press method and the calendar pressing method are especially preferred. Although press pressure in particular is not limited, 16 kg/cm² · 3 N/mm² are preferred. As for the pressing speed of the calendar pressing method, the amount of 0.1-50-mm is desirable. Room temperature 200 °C of press temperature is preferred.

[0043]The separator which can be used by this invention has the large degree of ion permeability to have a preferentialized mechanical strength, and what is necessary is just an insulating thin film, and as construction material, Cellofane system polymer, fluorine system polymer, cellulose type polymer, polyimide, nylon, glass fiber, and an alumina fiber are used, and a nonwoven fabric, textile fabrics, and a microporous film are used as a pestal. In particular, as construction material, the mixture of polypropylene, polyethylene, polypropylene, the mixture of polyethylene and polypropylene, and Teflon and the mixture of polyethylene and Teflon are preferred, and what is a microporous film as a pestal is preferred. In particular, the 5-50-micrometer thick microporous film whose aperture is 0.01-1 micrometer is preferred. Even if these microporous films are a dependent films, they may be uniaxial film which consist of more than two-layer (both which character, such as shape, density, all of a fine hole, and construction material, differs). For example, the composite film which consists the polyethylene film and the polypropylene film together can be mentioned.

[0044]Generally an electrolytes solution comprises a supporting electrolyte and a solvent. As for the

supporting electrolyte in a lithium secondary battery. Lithium salt is mainly used. As lithium salt which can be used by this invention, for example LiClO₄, LiBF₄, LiPF₆, LiDF₂CO₂, LiAsF₆, LiSbF₆, LiB₁₀F₁₈. The fluorosulfonic acid expressed with F_{2n+1}(SO₂)_n (n is six or less positive integer), the imide salt (n) expressed with LiN(SO₂C_nF_{2n+1})₂(SO₂C_nF_{2n+1}) the methide salt (p) as which n is expressed in six or less positive integer and LiC(SO₂C_nF_{2n+1})₂(SO₂C_nF_{2n+1})₂(SO₂C_nF_{2n+1})₂, respectively q and r, respectively six or less positive integer, low-grade aliphatic-carboxylic-acid lithium salt, such as LiAlCl₄, LiCl, LiBr, Li, chloroborane-lithium, and 4 phenyl lithium borate, can be used, and those kinds or two sorts or more can be mixed and used. When dissolved LiBF₄ and/or LiPF₆ especially is preferred. Although the concentration in particular of a supporting electrolyte is not limited, its 0.2-3 mol per l. of electrolysis solution is preferred.

[0105] As a solvent which can be used by this invention, propylene carbonate, ethylene carbonate, Butylene carbonate, chloroethylene carbonate, and trifluoromethyl ethylene carbonate, trifluoromethyl ethylene carbonate, and monofluoromethyl ethylene carbonate, Methyl hexafluorone acetate, methyl trifluoride acetate, dimethyl carbonato, Diethyl carbonate, trimethyl ethyl carbonato, gamma-hydroxybutanoic, Methyl formate, methyl acetate, 1,2-dimethylpropane, a tetrahydrofuran-2-methyltetrahydrofuran, dimethyl sulfide, 1,3-dioxolane, 2,2-bis(trifluoromethyl)-1,3-dioxolane, a furanone, Dimethylformamide, dioxolane, dioxane, acetonitrile, Nitromethane, ethylmmono-glyme, triethyl phosphate, toxic and flammable. Trimethoxy methane, a dioxolane derivative, sulfolane, 3-methyl-2-oxazolidinone, 1-alkyl sydnone alkyl groups are propyl, isopropyl, a butyl group, etc., a propylene carbonate derivative, a tetrahydrofuran derivative, ethyl ether. Aprotic organic solvents such as 1,3-propanediol, can be mentioned, and these kinds or two sorts or more are mixed and used. In these, the solvent of a carbonate system is preferred and it is preferred especially to mix and use cyclic carbonate and non-cyclic carbonate. As cyclic carbonate, ethylene carbonate and propylene carbonate are preferred. As non-cyclic carbonate, diethyl carbonate, dimethyl carbonate, and MECH₂CH₂CH₂LiK₂CO₃ETD⁺ are preferred. As an electrolysis solution which can be used by this invention, ethylene carbonate, propylene carbonate. The electrolysis solution which contains LiCF₃BO₃, LiClO₄, LiBF₄ and/or LiPF₆ in the electrolysis solution which mixed suitably 1,2-dimethoxyethane, dimethyl carbonato, or diethyl carbonato is preferred. Especially to at least one mixed solvents of propylene carbonate, at least one side of ethylene carbonate and dimethyl carbonate, or diethyl carbonate. A kind of salt selected from LiCF₃SO₃, LiCO₃, is LiBF₄ and the electrolysis solution containing LiPF₆ are preferred at least. The quantity in particular that adds these electrolysis solutions in a cell is not limited, but can be used according to the quantity of a positive electrode material or a negative pole material, or the size of a cell.

[0106] The forming solid electrolyte can also be used together besides an electrolyte solution. It is divided into an inorganic solid electrolyte and an organic solid electrolyte as a solid electrolyte. The

oxide of Li, the halogenide, the oxygen acid salt, etc. are well known by the inorganic solid electrolyte. Li₂N, Li₂, Li₂S, especially, Li₂N-LiOH, Li₂SiO₄, Li₂SO₄-LiOH, Li₂PO₄, Li₂X, Li₂SiO₃, Li₂SiE₂, a phosphorus sulfide compound, etc. are effective.

[0047]The polymer which contains a polyethylene oxide derivative or the derivative in an organic solid electrolyte. The polymer matrix material which made polymer containing a polyethylene oxide derivative or the derivative, polymer containing an ionic dissociation group, polymer containing an ionic dissociation group, the mixture of the above-mentioned acrylic electrolyte solution and phosphoric ester polymer, and an aprotic polar solvent contain is effective. There is also the method of adding polyacrylonitrile to an electrolyte solution. How to use together inorganic matter and an organic solid electrolyte is also known.

[0048]Other compounds may be added to an electrolyte in order to improve discharge and a charging and discharging characteristic. For example, pyridine, pyrrolidine, pyrrole, a trihexylamine, phenylethanolamine, Triethyl phosphate, Methanotetraene, cyclic ether, Ethylenediamine-n-glyme, hexane acid TORLAMIDO, a nitrobenzene derivative, Sulfox, a quinonimine dye, N-substitution oxazolidinone, and N and N'-substitution imidazolidinone, Ethylene glycol diethyl ether, quaternary ammonium salt, a polyethylene glycol, Pv1000, 2-methoxyethanol, AlCl₃, the monomer of a conductive polymer electrode active material, the triethylene-phosphonamide, trialkylphosphine, morpholine, The crown ether like an acyl compound and the 12-crown-6 and hexamethylphosphoric triamide with a carbonyl group, 4-alkyl morpholine, the bicyclic third class amine, oil of thyme, triphenyl phosphonium salt, the third class sulfonium salt, etc. can be mentioned. Especially a desirable thing is a case where it was independent, or number of and it uses, about a triphenylamine and phenylbarbazole.

[0049]In order to make an electrolyte solution into immobility, a halogen-containing solvent, for example, a carbon tetrachloride, and 2 fluoridation ethylene chloride can be included in an electrolyte solution, in order to give times to high temperature preservation, carbon dioxide can be dissolved in an electrolyte solution.

[0050]As for an electrolyte solution, it is desirable not to contain a part for moisture and free acid as much as possible. For this reason, as for the raw material of an electrolyte solution, what carried out sufficient drying and refining is preferred. Adjustment of an electrolyte solution has [the inside of dry air not more than minus 30 °C or inactive gas] the plateau dew point, 0.1-500 ppm of quantity for the moisture in an electrolyte solution and free acid is 0.2-100 ppm more preferably.

[0051]Although an electrolyte solution may pour in the whole quantity at once, it is preferred to pour in in 2 steps or more. When pouring in 2 steps or more, the prevention (after pouring in the solution which dissolved lithium salt in the nonaqueous solvent or the nonaqueous solvent, the solvent which dissolved lithium salt in the nonaqueous solvent or nonaqueous solvent whose viscosity is higher than said solvent is poured in) which is different site by the same polarization, may be sufficient as each liquid. It may perform decompressing a battery can for shortening of the injection time of an electrolyte solution, etc., or applying a centrifugal force and an ultrasonic wave to a battery

0052]The sheet board with which the battery can and battery lid which can be used by the invention performed the nickel plate as construction material, a stainless steel plate (SUS364, SUS304L, and SUS304HL) or a SUS316, SUS316L, SUS446, SUS444 grade, the stainless steel plate (same as the above) that performed the nickel plate, aluminum or its alloy, nickel, titanium, and copper, and is round shape tubed, ellipse form tubed one, square tubed, and rectangle tubed as shown. It is noted when an armor cast serves as a negative pole terminal, a stainless steel plate and the sheet board which performed the nickel plate are preferred, and when an armor can serve as a positive pole terminal, a stainless steel plate, aluminum, or its alloy is preferred. Any, such as a button, oval, a sheet, a cylinder, and an angle, may be sufficient as the shape of a battery can. A safety valve can be used for an exhaustion board as a measure against the internal pressure rise of a battery can. In addition, the method of putting in: setting can also be used for members, such as a battery can and a gasket. In addition, it may be equipped with various safety elements (a fuse, bimetal, a PTC element etc.) [For example, fast overcurrent-protection element known from the former]

[0053]Metal (for example, iron, nickel, titanium, chromium, molybdenum, copper, aluminum etc.) with electrical conductivity and those alloys can be used for the lead board used by the invention. A publicly known method (electric welding of an example, a direct current or exchange, laser welding, ultrasonic welding) can be used for the welding process of a utility lid, a battery can, an electrode sheet, and a lead board. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0054]As construction material, they are olefin system polymer, fluorine system polymer, cycloolefin type polymer, polyimide, and polyamide, from organic solvents-proof nature and low-water-flow part permeability, the gasket which can be used by the invention has preferred olefin system polymer, and especially its polymer of a propylene subject is preferred. It is preferred that it is block copolymerizable polymer of propylene and ethylene.

[0055]As for the cell assembled as mentioned above, it is preferred to perform aging processing. There are pre-treatment, activation, post-processing, etc. in aging processing, and the cell which was excellent in high charge-and-discharge capacity and cycle nature by this can be manufactured. Pre-treatment is processing for equalizing distribution of lithium in an electrode, and arbitrary combination of the temperature control for making dissolution control of lithium and distribution of lithium uniform, roasting and/or a rotating protans, and charge and discharge is performed, for example. Activation is processing for making lithium insert to the negative electrode of a cell proper, and it is preferred to insert 50 to 120% of the lithium insertion amount of the time of actual use charge of a cell. Post-processing is processing for fully carrying out activation, has this [for a judgment / charge-and-discharge processing], and can be arbitrarily combined with the storage processing for making a cell reaction uniform.

[0056]The desorption aging conditions (prefabrication condition) before activation of the invention are as follows. The temperature of not less than 30 °C to 70 °C or less is preferred, is more preferred, and is

still more preferred, [of not less than 40 °C 60 °C or less] [of not less than 30 °C 60 °C or less] As for open circuit voltage, less than more than 2.0V/3.0V is preferred, less than more than 2.5V/3.5V is more preferred, and less than more than 2.8V/3.3V is still more preferred. As for an aging period, 20 or less days will be preferred the 1st day or more, and especially its 15 or less days will be preferred the 1st day or more. As for the charge voltages of activation, more than 4.0V is preferred, less than more than 4.05V/4.2V is more preferred, and less than more than 4.1V/4.2V is still more preferred. As aging conditions after activation, less than more than 3.9V/4.3V has performed open circuit voltage, less than more than 4.0V/4.2V respectively is preferred, and the temperature of not less than 30 °C 70 °C or less is preferred, and is preferred, [of not less than 40 °C especially 60 °C or less] As for an aging period, 20 or less days will be preferred the 2nd day or more, and especially its five or less days will be preferred the 3rd day or more.

[0077] The cell of this invention is covered with a sheathing material if needed. As a sheathing material, there are heat shrinkable tubing, adhesive tape, a mylar film, paper, cloth, a paint, a plastic case, etc. The portion of the exterior discolored with heat in part at least is provided, and it may be made for a heat history to be known.

[0158] The cell of this invention constructs two or more in series and/or in parallel if needed, and is stored by the battery pack. A safety circuit (consist with the function when intercept current & the voltage of each cell and/or the whole cell group, temperature, current, etc. are monitored and it is required) besides safety elements, such as a high temperature coefficient resistor, a thermal cutout, a fuse, and/or a current cutoff element, may be established in a battery pack. The anode of each cell and a negative pole terminal, the whole cell group and the temperature detection terminals of each cell, the current detection terminal of the whole cell group, etc. can also be provided in a battery pack as an external terminal in addition to the anodic and negative pole terminal of the whole cell group. Voltage conversion circuits (DC-DC converter etc.) may be built in a battery pack. It may be by welding a lead board, and connection of each cell may be fixed so that it can detach and attach easily with a socket etc. Display functions, such as battery remaining capacity, existence of charge, and a use count, may be provided in a battery pack.

[0056] The unit of this invention is used for various apparatus. Especially A video movie, a portable videocassette recorder with a built-in monitor, a movie camera with a built-in monitor, it is preferred to be used for a digital camera, a compact camera, a single-lens reflex camera, a disposable camera, a notebook size personal computer, a note type word processor, an electronic notebook, a cellular phone, a cordless telephone, a headstrapped camber, a power tool, an electric mixer, a car etc.

[E sample] Although an example is named to below and this invention is explained in more detail, this invention is not limited to the example.

[008-1]As example 1 negative pore material, as a polyarylsilicon single substance (compound-1) and an alloy compound of the following compounded metalurgically Si-Ag alloy (compound-2) [Atomic ratio 35-70] the atomic ratio 60-40 and compound-3 the atomic ratio 80-20 and compound-

4). Si-aluminum fourcompounds-6 atomic ratio 80-40), Si-Ag-Cd (compound-8 80-30-10), Si-Zn fourcompounds-7 atomic ratio 80-40), Si-Au (compound-68 atomic ratio 80-40), Si-Ag-In fourcompounds-9 atomic ratio 80-30-10), Si-germanium (compound-10 atomic ratio 80-40), Si-Ag-Si (fourcompound-11 atomic ratio 80-30-10), Si-Ag-Sb (compound-12 atomic ratio 80-30-10). The silicon produced from Si-Ag-nickel (compound-13 atomic ratio 80-30-10) had Li₂Si unpoinded metallurgically by grinding the silicon which made Li melted 100% using hexaneplated in argon gas (compound-14), Si-SiO₂ (the compound-15 weight ratio 80-20) which used as the granular material the solid produced by mixing silicon and colored silica of compound-1 and heating at 1000 °C in the vibration mill in argon gas. Compound-16 The weight ratio 80-10 and compound-17 Weight ratio 80-430, Si-aluminum₂O₃ obtained using alumina sol in the similar way (compound-18 weight ratio 80-40). As the compound (compound-19 compound-2-SiO₂ weight ratio 80-10) to which SiO₂ was made to adhere by the method same to compound-2 as compound-16, and a compound plated with the non-electrolytic plating method in the silicon surface of compound-1. The silicon (as dextrin and a source of Ag, it is Ag₂O₂ as a reducing agent, atomic ratio 80-40 of compound-20 Si-Ag) which carried out Ag plating. Similarly nickel plating was carried out (as a reducing agent, it NaBH₄-Fe²⁺, and). As a source of nickel, NH₄Cl silicon atomic ratio 80-40 of compound-21 Si-nickel, the compound-22 atomic ratio 80-20, and compound-23 atomic ratio 30-70). The silicon (ZnO as NaBH₄ and a source of Zn as a reducing agent) (atomic ratio 80-40 of compound-24 Si-Zn) which similarly carried out Zn plating, it done after 30g's adding in the liquid which melted the compound (compound-25 compound-2-nickel weight ratio 80-20) polyvinylidene fluoride 3g which plated nickel with the electroless deposition method for compound-2 in 50 g of N-methyl pyrrolidone and carrying out the mix of the silicon of compound-1 to it. The granular material (compound-26) ground with the automatic mortar was used. The compound which covered polyvinylidene fluoride with the described method for compound-2 (compound-27 weight ratio 80-10 of compound-2-polyvinylidene fluoride). The compound which furthermore covered Ag with the non-electrolytic plating method for compound-14 (atomic ratio 80-40) of compound-28 Si-Ag). The compound which similarly covered nickel (atomic ratio 80-40 of compound-29 Si-nickel). The compound which covered polyvinylidene fluoride with the same method as compound-30 for compound-14 (compound-30Si-polyvinylidene fluoride weight ratio 80-10). The compound which covered nickel with the non-electrolytic plating method to compound-30 (ceri-pound-31 compound-30-nickel weight ratio 70-30). The compound which covered Ag with the non-electrolytic plating method for compound-15 (compound-32 wt. ratio 70-30 of compound-15-Ag). The compound (compound-33 wt. ratio 70-30 of compound-15-nickel) which similarly covered nickel, and the compound - weight ratio 80-10 of compound-34 compound-15-polyvinylidene fluoride similarly covered with polyvinylidene fluoride using compound-15 were used. The compound (compound-35 compound-34-Ag weight ratio 80-20) which covered Ag with the electroless deposition method for compound-34, the compound which similarly carried out nickel peeling (compound-36 compound-34-

Nickel weight ratio 80:20)

Each major grain size of the above-mentioned negative pole material compounds 1-3b) used the particles of the range of 0.05-4 micrometers. Next, it is N-methyl-2-pyrrolidone about 10 g of poly γ -vinylidene was added, the granular material produced by fully mixing acety nitrile graphite of same weight with the above-mentioned negative pole material (Compounds 1-3b) at 190 g and a binder, it distributed to 600 ml and the negative-electrode paste was created.

[0062] 5 g of poly γ -vinylidene is substantially mixed 200 g and 10 g of acetylene black with a homogenizer and mixed as a binder in positive-active-molecule LiCoO₂, and it is N-methyl-2-pyrrolidone, 600 ml was added, kneading mixing was carried out, and the positive electrode mixture paste was created.

[0063] Compression molding of the positive electrode mixture paste created above was carried out to both sides of the 30-micrometer-thick aluminum foil charge collector with the roller press machine after spreading and 100 °C ossification by the cold rolling machine. It judged in the pre-determined size, and the hard-like positive electrode sheet was created. Furthermore, drying desiccation was enough carried out with the far infrared heater all over the dry box (dew point: dry air not more than -50 °C), and the positive electrode sheet was created. Similarly, the negative electrode mixture paste was applied to a 20-micrometer copper foil charge collector, and the negative electrode sheet was created by the same method as the above-mentioned positive electrode sheet creation. The coverage of positive and negative poles adjusted the coverage of each electrode compound so that the charging capacity of the 1st cycle from which the charging capacity of the 1st cycle from which positive active material is set to 4.2V to a lithium metal, and the above-mentioned negative pole material one set to 0.0V might exist.

[0064] Next, the electrolysis solution was created as follows. By argon atmosphere, 95.3 g of diethyl carbonato was put into the polypropylene container of a 200-cc thin mouth, and 22.2 g of ethylene carbonato [\pm little] was dissolved every, taking care that solution temperature does not exceed 30 °C to this. Next, it dissolved in the above-mentioned polypropylene container every in small quantities in order, respectively, being careful of 0.4 g LiBF₄ and 12.1-g LiPF₆ for solution temperature not to exceed 30 °C. The obtained electrolysis solution was a water-white fluid by specific gravity 1.135. The amount of [18 ppm (it measures with a product made from Kyoto Electron Trade name: MKC-210 type Carl Pn. 5000 water measurement device) and 1 free acid of moisture was 24 ppm (the bromothymol blue is used as an indicator, and using a decimal NaOH aqueous solution, a neutralization titration is carried out and it is measured).

[0065] The cylinder cell was created as follows. How to make a cell according to drawing 1 is explained. The separator was laminated to the positive electrode sheet, the separator made from a microorous polyethylene film, and negative electrode sheet pair which were created above in order and this was spatially uttered around them. It signed to the iron closed-end cylindrical battery can (1) which performed nickel plating which serves this wound electrode group (2) as a negative pole terminal, and the top electric insulating plate (3) was inserted further, what laminated a positive pole

terminal (6), the insulating ring, the PTC element (83), the current cutoff object (82) and the pressure-induction valve element (81) after pouring in the above-mentioned electrolyte solution into the battery can -- a gasket (5) -- passing -- the cylindrical cell was created in total.